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Electrochemical reduction of cationic $Li^+@C_{60}$ to neutral $Li^+@C_{60}^{\bullet-}$: isolation and characterisation of endohedral [60]fulleride†

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Lithium-encapsulated [60]fullerene Li@C_{60}, namely, lithium-ion-encapsulated [60]fullerene radical anion $Li^+@C_{60}^{\bullet-}$, was synthesised by electrochemical reduction of lithium-ion-encapsulated [60]fullerene trifluoromethanesulfonylimide salt [$Li^+@C_{60}$]($TFSI^-$). The product was fully characterised by UV-vis-NIR absorption and ESR spectroscopy as well as single-crystal X-ray analysis for the co-crystal with nickel octaethylporphyrin. In solution Li@C_{60} exists as a monomer form dominantly, while in the crystal state it forms a dimer (Li@C_{60}–Li@C_{60}) through coupling of the C_{60} radical anion cage. These structural features were supported by DFT calculations at the M06-2X/6-31G(d) level of theory.

Introduction

Insertion of a metal atom into the fullerene cage is one of the most attractive methods to tune the electronic properties of a spherically π-conjugated fullerene carbon cage without changing the exterior framework. Ever since the resulting products, called "endohedral metallofullerenes (EMFs)", were reported[1] many studies on various EMFs have been conducted because of their unique electronic structure as a so-called "superatom"; formally defined by an electron transfer from the inner metal atom to the outer fullerene cage (Fig. 1a).[2,3] Among EMFs, which have various carbon-cage sizes, the C_{60}-based EMF has attracted special attention owing to its highly symmetrical structure and expected unique electronic properties.[4] However, the studies on metallo[60]fullerenes,[4,5] even the relatively well-studied alkali metal-encapsulated ones,[6] are somewhat stagnant due to the difficulty of their isolation and the lack of structural evidence.[7] Although some of us have reported the isolation of a lithium-ion-encapsulated [60]fullerene ($Li^+@C_{60}$) as a $SbCl_6^-$ salt [$Li^+@C_{60}$]($SbCl_6^-$) in 2010,[8] the isolated $Li^+@C_{60}$ is regarded as an "ion-encapsulated fullerene" which is a new endohedral fullerene family,[9] but is not categorised as part of general EMFs (Fig. 1b).

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† Electronic supplementary information (ESI) available: Ionic conductivity; solid state ESR spectrum; crystallographic table; MEM analysis; and DFT calculations. CCDC 1458690 and 1458691. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6sc01209d

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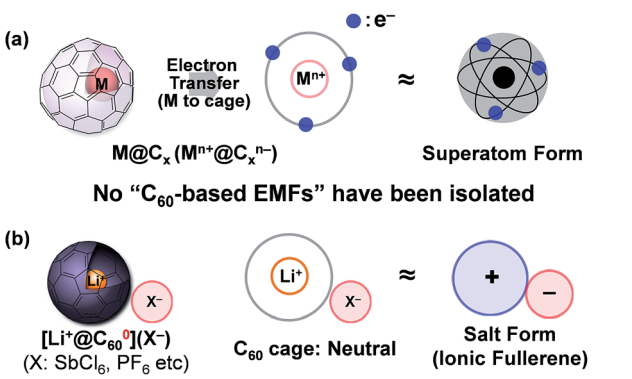

Fig. 1 Electronic state of (a) a general endohedral metallofullerene M@C_x, and (b) a lithium-ion-encapsulated fullerene [$Li^+@C_{60}$](X^-). The described electrons are derived from charge transfer from the encapsulated metal to the fullerene cage.

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Previously, we found that Li@C_{60}, namely, $Li^+@C_{60}^{\bullet-}$, was generated by the electrochemical reduction of $[Li^+@C_{60}](PF_6^-)$ in *o*-dichlorobenzene (*o*-DCB).[10] However, only a mixture of the product and the starting $Li^+@C_{60}$ salt was obtained. Purification of the product $Li^+@C_{60}^{\bullet-}$ has been a major challenge to achieve the first isolation of M@C_{60}. The ion-pair form of the [60] fullerene anion, named the fulleride, stabilised by an external counter metal or organic cations is an intriguing material because of their superconductivity[11] and magnetism.[12] The $Li^+@C_{60}^{\bullet-}$ can be deemed as an "endohedral [60]fulleride" as well as the simplest superatom. Thus, application of this material very promising in the organic electronics and materials chemistry fields.

We herein report the electrochemical reduction and complete isolation of $Li^+@C_{60}^{\bullet-}$ endohedral [60]fulleride by utilizing highly soluble $Li^+@C_{60}$ salt. We found that $Li^+@C_{60}^{\bullet-}$ forms Li@C_{60}–Li@C_{60} dimer in a co-crystal with nickel octaethylporphyrin (NiOEP), which was revealed by X-ray structure analysis and theoretical calculations. This is the first report of the isolation and unambiguous characterisation of a metal-encapsulated [60]fullerene consisted of only lithium and carbon atoms with a 100% encapsulation ratio.

Results and discussion

One of the major advantages of ionic $[Li^+@C_{60}](X^-)$ is that the solubility of the $[Li^+@C_{60}](X^-)$ salt can be modified by exchanging the counter anion (X^-) whereas the solubility of the other fullerenes could not be tuned without chemical functionalisation of the fullerene cage.[13] To prepare the target Li@C_{60}, we focused on the difference in solubility between the starting $[Li^+@C_{60}](X^-)$ salt and the product Li@C_{60}. After several attempts, lithium-ion-encapsulated fullerene bis(trifluoromethanesulfonyl)imide salt, $[Li^+@C_{60}](TFSI^-)$ was selected as the starting ionic fullerene because of its good solubility in CH_2Cl_2, which is a poor solvent for the product. $[Li^+@C_{60}](TFSI^-)$ salt was prepared by anion exchange from commercially available $[Li^+@C_{60}](PF_6^-)$ salt according to our previously reported procedure.[13] The electrochemical reaction was carried out under Ar atmosphere as depicted in Fig. 2. A CH_2Cl_2 solution of the starting compound was placed in an H-shaped cell, cooled to 253 K, and electrolysed using a Pt electrode at a constant current (0.5 μA) for 3 days. The purple solution gradually became colourless because of deposition of the reduced fullerene-based product on the surface of the cathode. In this process, due to sufficient ionic conductivity of the $[Li^+@C_{60}](TFSI^-)$ solution (see Fig. S1 in the ESI†), the electrochemical reaction could be carried out without any supporting electrolyte.

The obtained product was dissolved in *o*-DCB to be characterised by UV-vis-NIR and ESR, and NMR spectroscopy in the solution phase. The UV-vis-NIR spectrum of the product showed characteristic absorption at 1035 nm, which was assignable to the lithium-ion-encapsulated fullerene monovalent radical anion by a TD-DFT calculation (Fig. 3a and also see Fig. S2 in ESI†).[10,14,15] The ESR spectrum of the solution is shown in Fig. 3b. The observed *g* value (2.0010) was nearly identical to the reported value for the empty C_{60} radical anion and our previous results.[10,16] The ^{7}Li and ^{13}C NMR showed no signal due to the paramagnetic relaxation. The ^{19}F NMR spectrum of the product also showed no signals, indicating elimination of $TFSI^-$. These results suggest the absence of the starting $Li^+@C_{60}$ salt in the product and the complete isolation of neutral Li@C_{60}.

Conclusive structural evidence was obtained by X-ray structure analysis for a co-crystal of the product with NiOEP (OEP^{2-} = octaethylporphyrin dianion). The appropriate single crystal was obtained by electrochemical reaction in the presence of NiOEP, which is usually used as a cocrystallising agent for endohedral fullerenes.[17] Because of the much lower LUMO level of $Li^+@C_{60}$ than that of NiOEP, only the $Li^+@C_{60}$ was electrochemically reduced on the surface of the anode.[18] As shown in Fig. 4, the dimerised structure of $Li^+@C_{60}^{\bullet-}$ ($Li^+@C_{60}^-$–$Li^+@C_{60}^-$) connected by a single C–C bond was determined in the co-crystal. The dimer could be formed by the coupling of the spin centres of $Li^+@C_{60}^{\bullet-}$s, and this is not surprising because similar dimerization has been reported in alkali-metal doped fullerides,[19] a chemically reduced penta-arylated [60]fullerene derivative,[20] an open-shell EMF derivative,[21] and an anionic C_{60}^-–C_{60}^- dimer in the ionic charge-transfer complex of C_{60} with decamethylchromocene.[22] The equilibrium state of a C_{60} radical anion and its dimer in the solution phase and dimerization of the radicals in the solid phase has been already well-known,[23] and thus, in our case as well, the observed structure

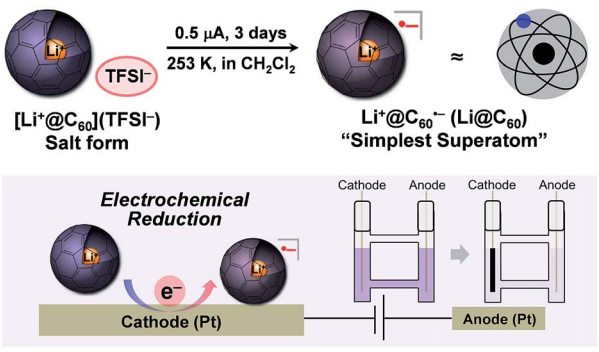

Fig. 2 Schematic image of the electrochemical one electron reduction of $[Li^+@C_{60}](TFSI^-)$ to Li@C_{60}.

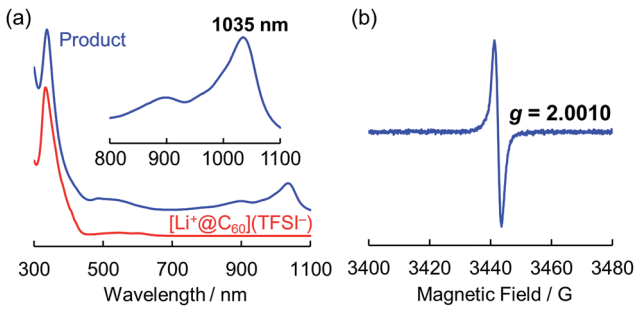

Fig. 3 (a) UV-vis-NIR spectra of product (blue line) and starting $[Li^+@C_{60}](TFSI^-)$ (red line) measured in *o*-DCB. (b) ESR spectrum of the product measured at 77 K in frozen *o*-DCB.

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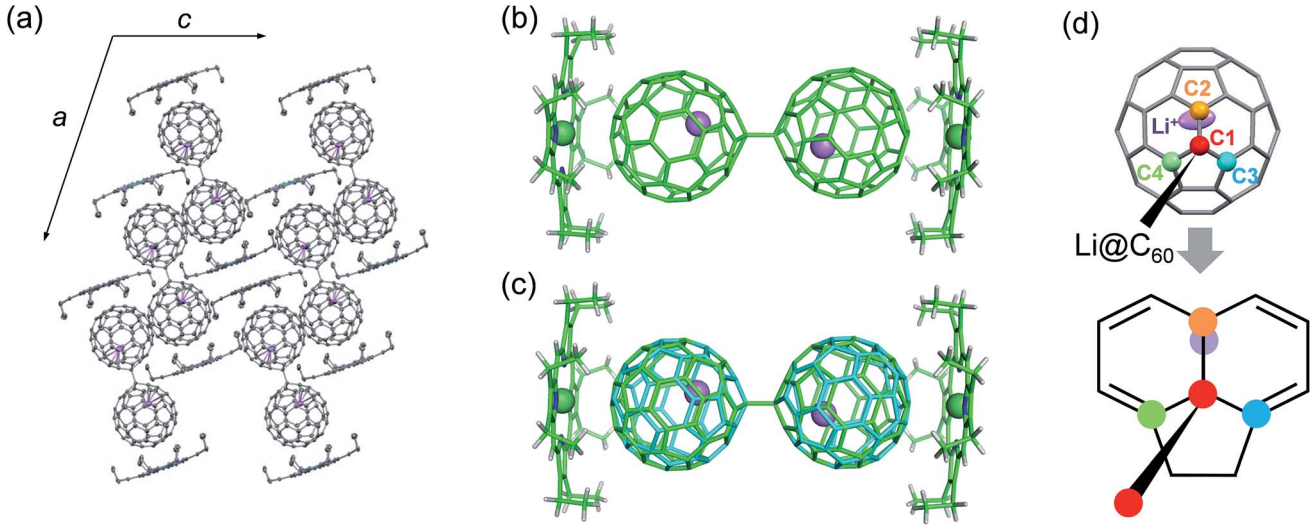

Fig. 4 Crystal structure of the $Li^+@C_{60}^{\bullet-}$–NiOEP co-crystal. (a) The molecular arrangement with thermal ellipsoids at the 50% probability level viewed along the *b*-axis at 100 K. Hydrogen atoms and dichloromethane solvent molecules are omitted in the Figure. (b) and (c) The $Li^+@C_{60}^-$–$Li^+@C_{60}^-$ dimer coordinated by two NiOEP molecules at 100 and 250 K, respectively. The $Li^+@C_{60}^-$–$Li^+@C_{60}^-$ dimer at 250 K is disordered by the overlapping of two molecules (green and blue) in a mirror relationship. (d) View along the single C–C bond connecting Li@C_{60}s. The four carbon atoms around the inter-fullerene single C–C bond are labeled as C1–C4. The length of each bond is 1.594(5) Å (C1–C1′), 1.528(5) Å (C1–C2), 1.546(6) Å (C1–C3), and 1.558(5) Å (C1–C4), respectively.

was attributed to an ion-pair form, $Li^+@C_{60}^{\bullet-}$, in the solution phase.

The $Li^+@C_{60}^-$–$Li^+@C_{60}^-$ dimer in the co-crystal at 100 K showed the *trans* conformation (Fig. 4b), which has been proposed by the X-ray powder diffraction study of the dimerised phase of AC_{60} fullerides and theoretical calculations of C_{60}^-–C_{60}^- and $(C_{59}N)_2$ as a stable conformation.[19,24] The length of a single C–C bond connected to each C_{60} cage (C1–C1′) was 1.594(5) Å, which was longer than the normal $C(sp^3)$–$C(sp^3)$ bond length (1.54 Å) and comparable to an interfullerene single C–C bond in the empty C_{60}^-–C_{60}^- dimer (1.597(7) Å).[22] Although it has been reported that the single C–C bond of the empty C_{60}^-–C_{60}^- dimer starts to break at 200–220 K in the crystal, our co-crystal did not show cleavage of the interfullerene bond up to 400 K and is stable in air. As shown in Fig. 4c, the $Li^+@C_{60}^-$–$Li^+@C_{60}^-$ dimer showed a disordered structure attributed to a ratchet motion of the C_{60}^- cage along the single C–C interfullerene bond with a rotating angle of about 39° at 250 K. The ratchet motion was induced in the high temperature phase through the phase transition around 250 K. The linear temperature dependence of the lattice constants with a small anomaly at the phase transition temperature suggests that the phase transition is of the order–disorder type (see Fig. S4 in ESI†).

The endohedral Li^+ was clearly observed, and localised near the carbon atom (C2) nearest to the carbon atom (C1) forming the interfullerene single C–C bond (Fig. 4d). The oxidation state of Li was estimated as +0.8(3) from the electron charge-densities which were obtained from the X-ray diffraction data by using the maximum entropy method (see Fig. S5 in ESI†). The result clearly indicated the formation of a "superatom state" as in reported EMFs, and coincided with the results of ESR spectroscopy. The C1 carbon atom bonded with the C2 carbon atom by a short 6 : 6 bond fusing two hexagons, and C3 and C4 carbon atoms bonded by a long 6 : 5 bond fusing a hexagon and a pentagon. The C1–C2, C1–C3 and C1–C4 bond lengths were 1.528(5), 1.546(6) and 1.558(5) Å, respectively, which were much longer than the 6 : 6 and 6 : 5 bond lengths for neutral C_{60} (1.39 and 1.45 Å, respectively),[25] and comparable to the normal $C(sp^3)$–$C(sp^3)$ bond length (1.54 Å). These results indicate that the C2 atom bonded to the C1 atom by the shorter 6 : 6 bond has excess electrons, and the excess electrons attract the encapsulated Li^+, causing the localisation of the Li^+ near the C2 atom. The Li–C2 distance was 2.20(1) Å at 100 K. The Li–C distance was shorter than that of 2.344(6) Å in a cubic $[Li^+@C_{60}](PF_6^-)$ crystal around 25 K, in which the Li^+ equivalently localizes under the centres of two hexagons on the three-fold inversion axis by the electrostatic interaction from the coordinated six PF_6^- anions.[26] The ion-pairing with the short Li–C bond contributes to the stabilisation of the anionic C_{60} cage bonded by the single C–C bond in the $Li^+@C_{60}^-$–$Li^+@C_{60}^-$–NiOEP co-crystal.

We also performed X-ray diffraction measurements for the powder sample of $Li^+@C_{60}^{\bullet-}$ resulting from electrolysis of $[Li^+@C_{60}](TFSI^-)$ (see Fig. S6 in ESI†). Unfortunately, the sample had a more complicated crystal structure and/or contained multiple phases, and thus indexing of the powder diffraction pattern with a single phase by using *DICVOL*[27] was unsuccessful. Incidentally, the powder sample also showed a similar ESR signal to that measured in frozen *o*-DCB (see Fig. S3 in ESI†), which indicated that while the Li@C_{60} dimer could be formed perfectly in a well-ordered crystal, the $Li^+@C_{60}^{\bullet-}$ monomer remained partially in the disordered solid state.

The observed equilibrium behaviour of the $Li^+@C_{60}^{\bullet-}$ monomer and its dimer was consistent with the results of DFT

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calculations at M06-2X/6-31G(d) level of theory (Fig. 5). An estimation of the change in Gibbs free energy (ΔG) of dimerization of $Li^+@C_{60}^{\bullet-}$ in *o*-DCB was made using the SCRF(IEFPCM) methodology. The results revealed that while the formation of singlet dimer was energetically favourable in vacuum ($\Delta G = -4.35$ kcal mol^{-1}), $Li^+@C_{60}^{\bullet-}$ monomer was slightly stable in *o*-DCB solution ($\Delta G = +0.29$ kcal mol^{-1}), which indicated the higher stability of the $Li^+@C_{60}^{\bullet-}$ monomer as a result of the surrounding solvent molecules in the solution phase.[28] We also calculated the ΔG of dimerization of the empty C_{60} radical anion in *o*-DCB using the same method, and the value was calculated to be +11.5 kcal mol^{-1} (see Fig. S7 in ESI†), which was higher than that of $Li^+@C_{60}^{\bullet-}$. The difference could be explained by the degree of electrostatic repulsion between anionic fullerene spheres relaxed by the unique ion-pair form in the endohedral fullerides. In $Li^+@C_{60}^{\bullet-}$, the positional relation between an encapsulated Li^+ ion and an anionic C_{60} must be nearly constant because Li^+ cannot be released from the anionic cage. The effect of solvation is known as important factor when the electrostatic interaction is considered,[29] but the solvation may not be important for such a unique shielded ion. Thus the negative charge on the anionic C_{60} cage might be cancelled more effectively by the "perfect" ion pairing of the internal Li^+ ion and the negative charge on the C_{60} cage, which makes the electrostatic repulsion force between $Li^+@C_{60}^{\bullet-}$s weaker. Nevertheless, as we already mentioned, the $Li^+@C_{60}^{-}$–$Li^+@C_{60}^{-}$ dimer was not observed in *o*-DCB solution by any spectroscopic analyses, which indicated that majority of the $Li^+@C_{60}^{\bullet-}$ exists as a monomer at ambient temperature in the solution phase.

$Li^+@C_{60}^{\bullet-}$ and its dimer are also interesting in terms of their quasi-atomic/molecular electronic structure. Because the $Li^+@C_{60}^{\bullet-}$, consisting of encapsulated monocationic Li^+ and a nearly spherical anionic C_{60} cage with a single unpaired-electron, is very similar to the nucleus and orbital of a hydrogen atom, $Li^+@C_{60}^{\bullet-}$ can be considered as the "simplest" superatom. Through the dimerization of $Li^+@C_{60}^{\bullet-}$, in addition, the superatomic structure converts to the model of a "pseudo homonuclear diatomic molecule", again like a hydrogen molecule. The unique structure of the superatomic molecular orbital of doped C_{60} has been predicted only by theoretical calculation.[30] Thus, the present $Li^+@C_{60}^{\bullet-}$ will play an important role as a simplest example of a superatom, providing a unique model of the molecule-like orbital structure.

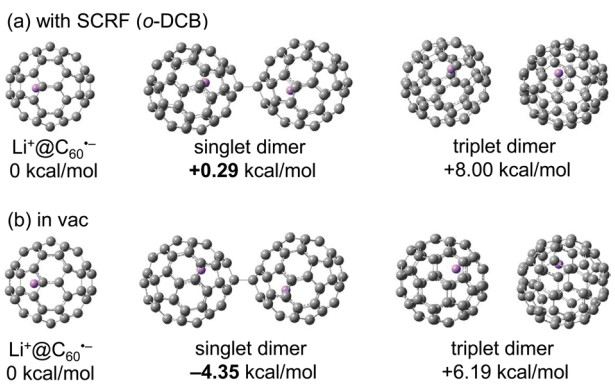

Fig. 5 Change in Gibbs free energy of dimerization of $Li^+@C_{60}^{\bullet-}$ calculated by DFT (M06-2X/6-31G(d)) (a) using the SCRF(IEFPCM) methodology and (b) in vacuum.

Conclusions

In summary, we have successfully isolated the lithium-ion-encapsulated fullerene radical anion $Li^+@C_{60}^{\bullet-}$, which can be considered as a general EMF form of lithium-encapsulated fullerene $Li@C_{60}$, by means of the electrochemical reduction of ionic $[Li^+@C_{60}](TFSI^-)$. Due to the solubility difference between ionic $Li^+@C_{60}$ and the $Li^+@C_{60}^{\bullet-}$ superatom, only the product was deposited on the surface of the electrode. Thus, we did not need to purify the product by common methods for the purification of metallofullerenes such as the preparative HPLC technique. The product was unambiguously characterised by spectroscopic analyses as well as X-ray structure analysis for the co-crystal with NiOEP. The $Li@C_{60}$ exists dominantly as a monomer form, while in the crystal state it forms a dimer ($Li^+@C_{60}^{-}$–$Li^+@C_{60}^{-}$) through coupling of the radical centre on the anionic C_{60} cage. These structural features were supported by DFT calculations at the M06-2X/6-31G(d) level of theory. This is the first report of the isolation and characterization of a [60] fullerene-based metallofullerene. With this detailed structural information and great anticipation for the expected unique properties, utilisation of this new metallofullerene for various applications may be possible.

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